

$\Delta^{17}\text{O}$ measurements of carbonate from ALH84001: Implications for oxygen cycling between the atmosphere-hydrosphere and pedosphere of Mars. J. Farquhar, M.H. Thieme, and T. Jackson, Department of Chemistry, The University of California San Diego, 92093 (jfarquha@ucsd.edu).

Here we report measurements of ^{16}O , ^{17}O , and ^{18}O in carbonate minerals from ALH84001. These measurements can be reconciled with previously reported measurements of $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and δD for water and silicate minerals¹⁻³, $\delta^{18}\text{O}$ for carbonate minerals^{4,5}, and measurements of the present-day martian atmosphere⁶ to gain insight into past atmosphere-hydrosphere-pedosphere interactions on Mars and processes that have occurred to control the oxygen chemistry within the Martian atmosphere.

Methods

Approximately 200 mg of sample material from ALH84001.137 was coarsely ground and was loaded into a side-arm reaction vessel containing 100% H_3PO_4 ($\rho=1.932\text{g/cc}$). The sample was outgassed at room temperature for 7 days, and then reacted at 25.1 °C for 24 hrs. 1 micromole of gas was extracted from this step and transferred to a break-seal. The sample was then heated to 150 °C in an oil bath for three hours while connected on-line to a liquid N_2 -chilled trap. 6.5 micromoles of condensable gas were evolved in this reaction and separated from water at – 80 °C.

The second aliquot of condensable gas was purified by freezing it into the inlet of a Varian 3600 gas chromatograph equipped with an 8' long, 1/8" id, packed Alltech Hayesep Q column at 30 °C with a He-carrier gas flow rate of 20 ml/min. The gas chromatograph is mated to a high-vacuum, gas-handling and separation line by a 10' length of 0.020" id capillary tubing to allow continuous and simultaneous operation of the GC and the high-vacuum line. CO_2 produced by acidification of meteorite samples may be heavily contaminated with S-bearing gas species such as H_2S . The gas chromatograph allows separation and purification of these species. Control experiments show collection efficiencies within uncertainty of 100% with no isotopic fractionation associated with this purification step. Approximately 5.7 micromoles of CO_2 were extracted from the condensable fraction of gases liberated by the 150 °C acidification step. The H_2S was reserved in a break seal for S-isotope analyses.

The purified CO_2 was transferred to a Ni reaction tube. 100 times excess amount of precooled (120 minutes at 800 °C) BrF_5 was added to the tube. The mixture was then heated for 45 hours at 800 °C⁷. The reaction produces O_2 , CF_4 , and a number of condensable Br and BrF compounds. O_2 and CF_4 are condensed at liquid N_2 temperatures for 76 minutes onto the leading edge of a U-trap filled with molecular sieve 13X (60/80 mesh). O_2 is purified by raising the temperature of this trap to –116.5 °C and by pumping into a second trap (also filled with molecular sieve 13X) at liquid nitrogen temperature for 68 minutes. This procedure re-

duces the concentration of CF_4 by more than three orders of magnitude and also eliminates NF_3 .

The $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ were measured in three cycles of ten measurements at m/e 32, 33, and 34 using a Finnigan MAT 251. This gives uncertainties on $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ resulting from the mass spectrometer measurement of 0.02 and 0.05 ‰ (std error). Uncertainties on the entire procedure for this size sample are estimated to be better than ± 0.4 ‰ for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$. $\Delta^{17}\text{O}$ is the magnitude of the difference of a measured datum relative to the terrestrial fractionation line which is given by the empirical power law relationship¹:

$$(1+\delta^{17}\text{O}/1000)=(1+\delta^{18}\text{O}/1000)^{-52}$$

Uncertainties in $\Delta^{17}\text{O}$ are of the same order, or smaller than the uncertainties on for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ from the mass spectrometer because for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are highly correlated and also because fractionations introduced by the chemical procedures that we use are mass dependent (i.e. $\delta^{17}\text{O} \sim 0.52 \delta^{18}\text{O}$).

Results and Discussion

Our measurements of carbonate from ALH84001 give $\delta^{18}\text{O} = 18.3$ ‰ and $\delta^{17}\text{O} = 10.3$ ‰ and $\Delta^{17}\text{O} = 0.8$ ‰. These values were calculated assuming the same fractionation factor for the acidification procedure as that measured for acidification of siderite at 150 °C ($\alpha=1.00771$)⁸. The fractionation factor for ^{17}O was assumed to be $\alpha^{0.52}$. Three measurements of SRM NBS-18 yielded $\delta^{18}\text{O} = 6.8 \pm 0.4$ ‰ and $\delta^{17}\text{O} = 3.6 \pm 0.4$ ‰ and $\Delta^{17}\text{O} = 0.05 \pm 0.03$ ‰. The accepted value of SRM NBS-18 is 7.16 ‰.⁹

Previous measurements of $\delta^{18}\text{O}$ for carbonates from ALH84001 range from –9 to 22.6 ‰ with the bulk of analyses falling between 9 and 22.6 ‰^{4,5}. Measurements of SNC silicate minerals indicate that $\Delta^{17}\text{O}$ is 0.22 ‰ for ALH84001, and between 0.21 and 0.38 ‰ for other members of SNC meteorites¹. Karlsson et al.² measured water extracted by pyrolysis of a number of SNC meteorites and found that $\Delta^{17}\text{O}$ was variably enriched, ranging from terrestrial values near 0 to > 0.8 ‰. The importance of this latter observation is that it indicates that the waters were not in equilibrium with the silicate rocks, implying that the atmosphere was out of oxygen isotope equilibrium with the lithosphere. Subsequent to the Karlsson et al.² study, Leshin et al.³ compared H/D results of pyrolysis experiments on the same meteorites, also ALH84001. Although they found correlations between some of their hydrogen results and some of the Karlsson et al.² results the correspondence was imperfect. The shergottites exhibited large δD anomalies but no $\Delta^{17}\text{O}$ anomaly, the nakhlites exhibited anomalies in both systems, and Chassigny exhibited a large $\Delta^{17}\text{O}$ anomaly but little distinguishable difference between δD and terres-

trial values. Our measurements of carbonate from ALH84001 indicate that ALH84001 also preserves evidence for oxygen isotope disequilibrium between the atmosphere and the lithosphere and are consistent with the results of D/H measurements by Leshin et al.³. Valley et al.⁴ indicate that fine-scale oxygen isotope heterogeneity are preserved by these carbonates and, therefore, that significant post-growth isotopic reequilibration did not occur. Our findings extend the atmospheric anomaly to the time of carbonate growth.

That the anomaly is present in both water and carbonate reflects the precipitation of carbonate from water. It also is in keeping with high rates for oxygen exchange between water and carbon dioxide – major components of Mars's hydrosphere and atmosphere.

The fact that oxygen isotope disequilibrium is found in some meteorites and not in others suggests that the oxygen isotope composition of the Martian atmosphere has been out of equilibrium with the lithosphere at several times in Martian history. A critical question in assessing the oxygen and hydrogen isotope data for water is its relationship to the atmosphere. I.E. Whether hydrogen and oxygen isotopes are coupled during atmosphere-hydrosphere-lithosphere interactions. The H:O abundance ratio of the hydrosphere is significantly different than that of the lithosphere. Therefore, it may be possible to decouple hydrogen and oxygen isotope systematics in much the same way that they are decoupled in meteoric hydrothermal systems¹⁰. Consequently, the $\Delta^{17}\text{O}$ vs δD relationships may reflect different conditions of fluid-rock interaction, and the $\Delta^{17}\text{O}$ atmospheric anomaly indicated by the waters² and carbonate data may have been maintained at a relatively constant state throughout a significant part of Mars's geological history.

On Earth, plate tectonics cycles water from the hydrosphere, through the mantle, providing a process through which the much larger oxygen reservoir of the mantle buffers the oxygen isotope systematics of the hydrosphere¹¹. It has been previously noted that the lack of plate tectonics on Mars significantly reduces the efficiency of this mechanism for homogenizing these two oxygen isotope reservoirs². The lack of a homogenizing process is critically important for models of atmospheric evolution that attribute the oxygen isotope disequilibrium to late impactors, or early atmospheric escape^{2,12}.

Photochemical reactions provide a mechanism for generating a steady-state oxygen isotope anomaly in the Martian atmosphere independent of homogenizing processes. When the oxygen budget of the hydrosphere is dominated by atmospheric exchange, the anomaly would be transferred to the hydrosphere.

On Earth, there is ample evidence for mass-independent oxygen isotope fractionations involving stratospheric CO_2 . Also, a large number of gas-phase photochemical reactions have been found to impart mass independent isotope fractionations¹³. The principal requirement is the wavelength of radiation required for the chemistry and the presence of O_3 and CO_2 . Due to the thinness of the atmosphere, O_3 is present at the Martian surface. Ozone is well known to occur in the Martian atmosphere.⁶ Many reactions may have contributed to the observed mass independent oxygen isotope fractionations in meteoritic waters and carbonates. We suggest that the predominant reactions responsible for producing the observed anomaly were:

- (1) $\text{CO}_2 + h\nu = \text{CO} + \text{O}$
- (2) $\text{O} + \text{O} = \text{O}_2$
- (3) $\text{O}_2 + \text{O} + \text{M} = \text{O}_3 + \text{M}$
- (4) $\text{O}_3 + h\nu = \text{O}(^1\text{D}) + \text{O}_2$
- (5) exchange rxn $\text{O}(^1\text{D}) + \text{CO}_2 = \text{CO}_3^* = \text{CO}_2 + \text{O}$
- (6) exchange rxn $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$

The source of the isotopic anomaly is reaction (3), which has an associated fractionation of $\sim 100\%$ in both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, reaction (4) which transfers this anomaly to $\text{O}(^1\text{D})$, and reaction (5) which is the exchange reaction between $\text{O}(^1\text{D})$ and CO_2 .

References

- ¹Clayton and Mayeda, 1983 GCA, 62, 1; 1996 GCA 1999.
- ²Karlsson et al., 1992 Science 255 1409
- ³Leshin et al., 1996 GCA, 61, 2635.
- ⁴Valley et al., 1996 Science 275, 1633.
- ⁵Romanek et al, 1994 Nature, 372 655, Jull et al., 1995 Meteoritics 30 311
- ⁶Clancy et al., 1996 JGR 101 12777.
- ⁷Clayton and Mayeda, 1963 GCA, 27, 43. ; Bhattacharya and Thiemens, 1989)
- ⁸Rosenbaum and Sheppard, 1986 GCA 50 1147.
- ⁹Coplen et al 1983 Nature 302 236.
- ¹⁰Criss and Taylor MSA Rev Mineral, 16, 373.
- ¹¹Muehlenbachs and Clayton, 1976 JGR 81, 4365.,
- ¹²Jakoski 1993 GRL, 20, 1591.
- ¹³Heidenrich and Thiemens 1983 J. Chem Phys 84, 2129; Wen and Thiemens 1993, JGR 98 12801; Yung et al. 1997 JGR 102, 10857.